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3,594,172

LIGHT DEVELOPABLE, DIRECT-WRITING, SILVER HALIDE EMULSIONS CONTAINING GOLD AND IODINE

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ABSTRACT OF THE DISCLOSURE

Light-developable, direct-writing, radiation-sensitive silver halide emulsions, emulsion layers and elements containing molecular iodine or an iodide ion-yielding compound, a gold salt and optionally a water-soluble bromide and/or plumbous salt, and process for recording images.

This application is a continuation-in-part of my co-pending application Ser. No. 588,734 filed Oct. 24, 1966 now abandoned.

BACKGROUND OF INVENTION

Field of the invention

This invention relates to direct-writing or printing, light-developable oscillographic recording elements, e.g., films or papers, and to image-recording processes.

Description of the prior art

Radiation-sensitive elements adapted for light-recording, e.g., oscillographic recording, are known. They have slow speed, require long access time and have low image density. In addition, they lack image stability under ambient light conditions and are not developable by conventional chemical developing solutions. Proposals have been made to produce improved direct-writing elements. One proposal is disclosed in Hunt U.S. Pat. 3,249,440, May 3, 1966, where the silver halide emulsion layers contain molecular iodine. These layers have good direct-writing speeds and improved sensitometric characteristics as compared with the prior art.

In accordance with this invention, improved, light-developable, direct-writing emulsions can be made by admixing (1) an emulsion of light-sensitive silver halide grains having an average particle size in the range 0.1–10.0 microns and a water-permeable macromolecular organic colloid binder, (2) molecular iodine or an iodide ion-yielding compound in the amount of 0.05–15 mole percent, preferably 0.8–10 mole percent and (3) a gold compound in an amount 0.0005–1.0 mole percent, preferably 0.01–0.2 mole percent, all based on silver halide.

The resulting light-developable, direct-writing silver halide emulsion has higher maximum density and better image stability than when molecular iodine is used without the gold compound. Writing speed is substantially increased and the contrast improved. Background densities are lower and the light-development or photolysis time necessary for the first image appearance is reduced substantially. The direct-writing elements of this invention are also capable of being chemically developed with conventional developing solutions and can also be made

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to produce reversed images when desired. That is, instead of a dark oscillographic trace on a light background, it is possible to produce a white trace on a dark background.

The photosensitive elements of this invention can be photodeveloped for the direct-writing effect and can then be processed in a conventional photographic developer solution such as that shown in Example IV below to give a permanent black and white positive image. The speed of this reversed image is at least as high as the direct-writing or direct print-out image. Thus, more information is achieved than by development of the negative image where conditions have to be kept under photographic safelights until the paper is fixed.

The negative image development is catalyzed by the surface latent image. The halogen acceptors used under the preferred conditions do not fog and clean images of high contrast result. The sensitivity is lower than in dry direct-writing emulsions because the latter utilize the internal sensitivity and these emulsions are designed to enhance internal sensitivity at the expense of surface sensitivity.

Photodevelopment exposure causes the internal latent image to become visible. The positive holes generated at this second exposure oxidize the surface latent image and no surface catalysis for development remains in the image area. The background, however, forms latent image centers during this second exposure. Upon development, a positive image forms. The modulating effect in this process is the internal latent image of the first exposure. Therefore, the direct writing and reversed images have the same speed.

This invention also provides a new class of direct writing emulsions which have an unexpected, unique, and useful characteristic which may be termed "autolatensification." Latensification (latent image amplification) can be defined as the treatment of an exposed radiation-sensitive element after image exposure but before development. Chemical latensification is well known in the conventional photographic art, where various processing baths have been employed before development to increase speed and contrast of wet developed images (Mees and James, "The Theory of the Photographic Process," 3rd ed., The Macmillan Co., New York, 1966, chapter 16).

The Mees textbook recognizes that latent image formation is a stepwise process. It is believed that the initial quantum absorption in silver halide produces an unstable sublatent image center which is then converted to a stable sublatent image center and finally to a developable latent image as more quanta are absorbed. The high intensity-short duration photon burst employed in direct writing exposures produces all three types of image centers. The fate of these image centers, when they are subsequently exposed to the photolytic radiation employed to render the image visible, depends on their size. This secondary exposure not only causes the latent image to grow to visibility through the aggregation of photolytic silver, but also bleaches sub-latent image centers through solarization, Herschel phenomena, and Villard reversal. This latent image disappearance results in speed and contrast loss.

Hunt, U.S. 3,183,088, teaches light latensification of direct-writing latent images in optically sensitized direct writing emulsions. After the imaging exposures, Hunt irradiates such elements with light in the spectral region of extra sensitivity conferred to the silver halide emulsion

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by the sensitizing dye before photodeveloping the latensified element with actinic radiation. It is believed that in this latensification process the absorbed light quanta excite the dye molecules which then transfer electrons (or energy) to the silver halide grain. This has the same effect as electrons excited into the conduction band during direct absorption by the silver halide. In this latensification process at taught by Hunt, however, no positive holes (halogen atoms) are generated within the grain, so little or no bleaching of sub-latent image centers can occur. The sub-latent and latent image centers grow sufficiently so that no image destruction occurs during the subsequent development by actinic radiation. The net result is a gain in speed and density.

The autolatensification which occurs in silver halide emulsions made according to this invention is a dark reaction which takes place in the absence of actinic radiation and is not completely understood. Apparently, a stable but active gold-iodine complex is present on or near the silver halide grain surface. As soon as an imaging exposure is made, this complex transfers electrons to the grain which stabilize or enlarge the latent image centers. The autolatensification is a kinetic process and is time and temperature dependent. Image density and photographic speed are proportional to the time interval between image exposure and the initiation of photolysis. Autolatensification is rapid, occurring within 1-180 seconds. At room temperature, significant latensification occurs in 30 seconds or less, approximately 3 minutes sufficing for an essentially maximum gain in speed and density. At 200° F., the time required for maximum autolatensification is of the order of one second. The process is sensitive to actinic light; autolatensification is inhibited by photolytic exposure immediately following the imaging exposure.

The autolatensification is independent of the light latensification described by Hunt. If the Hunt process is carried out with optically sensitized emulsions of this invention, the Hunt latensification and autolatensification are complementary. This indicates that the latensifying actions are similar. Hunt injects electrons into the silver halide conduction bands from excited dye molecules. For this invention, the electron source is the active iodine-gold moiety. It is obvious that modern oscillographs can be modified readily to permit of a short period between image exposure and photolysis during which the photographic material is held or transported in the absence of actinic radiation either at room temperature or at moderately elevated temperatures for a time interval of at least 0.1 second to increase speed and contrast through autolatensification.

The oscillographs can be modified to include a dark chamber or light-blocking partitions and may contain heating element in the dark areas. It is also desirable that a graduated increase to photolyzing light be employed. This tends to prevent a build-up of background density or fog. This may be accomplished by means of light filters of varying density.

The value of increased speed and contrast in photo-recording is readily apparent.

SUMMARY OF THE INVENTION

The light-developable, direct-writing, radiation-sensitive silver halide emulsions, layers and elements of the invention contain 0.05-15 mole percent of molecular iodine or an iodide ion-yielding compound, 0.0005-1.0 mole percent of a water-soluble gold salt, and optionally up to 120 mole percent of a water-soluble bromide and/or up to 5 mole percent of a water-soluble plumbous salt. The processes of the invention comprise exposing the emulsion layer to a light imaging source and preferably holding the exposed layer from exposure to actinic radiation for a short period. During this holding period, heat may be applied to facilitate autolatensification. The exposed element is then photodeveloped by exposure to actinic radiation.

In making the silver halide emulsion, it is preferable to add at least one water-soluble halide, e.g., lithium, sodium, potassium, calcium, magnesium or ammonium halide (preferably KBr) to the final emulsion in an amount in excess of that necessary initially to precipitate all silver as silver halide.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The light-developable, direct-writing, light-sensitive emulsions and emulsion layers of this invention comprise an emulsion or dispersion of radiation-sensitive silver halide grains having an average grain size in the range 0.1-10 microns in a water-permeable macromolecular colloid having protective colloid properties, said emulsion containing, based on the silver halide:

- (a) 0.05-15 mole percent of molecular iodine or an iodide ion-yielding compound, preferably 0.8-10 mole percent,
- (b) 0.0005-1.0 mole percent of a gold salt, preferably 0.01-0.2 mole percent,
- (c) 0-120 mole percent of a water-soluble bromide, and/or
- (d) 0-5 mole percent of a water-soluble plumbous salt.

The silver halide emulsions of this invention are preferably of the silver bromide or silver chlorobromide type, but other types, i.e., chloride, iodobromide, etc., can be used. Suitable emulsions are described in Hunt U.S. 3,249,440. The background density, image density, and image stability of the emulsion layers depend on the silver halide or halides employed and, where necessary, can be improved by the use of any of the specific plumbous salts and specific soluble bromides disclosed in Bigelow U.S. 3,178,293. Bigelow incorporates the plumbous salt with the aqueous silver nitrate used in precipitating the silver halide. The silver halide may be precipitated in a known manner, e.g., by slowly adding an aqueous solution of silver nitrate and a water-soluble plumbous salt to an acidified aqueous solution of a water-soluble halide or halides containing a water-soluble dispersing agent, e.g., gelatin. Where soluble chloride salts are used, it is desirable because of solubility differences, to form the silver halide grains of desired composition and size and then add sufficient soluble bromide salts to provide the desired concentration of bromide ions. When it is desired, other halides or combination of halides may be used to form the silver halide grains. For example, pure silver chloride, chlorobromide or iodobromide may be used.

In Hunt 3,249,440, there are described a list of suitable water-soluble silver salts and water-soluble halides all of which can be used, in accordance with this invention, to make the silver halides. The specific water-soluble bromides listed in the Hunt patent also can be used as constituent (c).

Among the useful gold salts one can use gold halides, e.g., auric chloride, bromide or iodide or complex gold halides such as potassium or sodium auric chloride, bromide or iodide, sodium or potassium aurous chlorides, bromides or iodide, auric sulfate, complex gold salts such as potassium aurothiocyanate, aurous thiosulfates, alkali metal aurous sulfates and complex salts as are formed between thiourea and auric chloride, thiosinamine and auric chloride, etc. In addition, organo-metallic compounds can be used which decompose in the strongly complexing media of silver halide emulsions to yield the simpler gold salts described above. One or more of the gold compounds may be used.

As suitable iodide ion-yielding compounds, there may be used the alkali, ammonium and alkaline earth metal iodides. However, other metal iodides may be used, even relatively insoluble compounds such as plumbous iodide since those will react with silver bromide by double decomposition because of the extreme insolubility of silver iodide. Similarly, certain organic iodides will yield iodide ion when incorporated in the silver halide emulsions of

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this invention through hydrolysis or metathesis reactions, e.g., acyl, alkyl and quaternary amine iodides.

After precipitation and ripening, the emulsion usually is washed. Washing may be done as described in Moede U.S. 2,772,165. The emulsion is then redispersed and may be digested in a usual manner. At this stage or prior to digestion, optical sensitizers may be added to increase the spectral response of the emulsion for use in instruments employing a variety of light sources. There is then added from 0.05 to 15 mole percent of molecular iodine or an iodide ion-yielding compound, based on the silver halide, is added with from 0.0005 to 1.0 mole percent, based on the silver halide, of a gold salt. A plumbous salt may also be added as described in Hunt U.S. 3,033,682. After such steps, materials, e.g., hardeners, wetting agents, etc., can be added and the viscosity adjusted, as desired, by addition of more gelatin or other colloid. In general, the ratio of gelatin to silver halide is 1:1, however, it is not at all critical. The pH of the emulsion at coating may vary from 1 to 10.0. The final emulsion is then coated on a suitable support, e.g., paper, and dried. Usually a dry coating weight equivalent to about 30 mg. AgBr/dm.² is satisfactory.

To determine the sensitometric characteristics of the layer, it may be exposed through a 21-step $\sqrt{2}$ step wedge in an electronic flash sensitometer (Edgerton, Germeshausen and Grier (E.G.&G.) Mark III, VI or VII model). This type of instrument uses a xenon discharge tube as a source of radiation and has available exposure times of 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} , and 10^{-6} seconds. Relative sensitivity of layers measured with this instrument can be stated as the number of steps recorded in the image. The exposed layer may be light-developed by irradiation with ordinary room lighting or with an ordinary fluorescent lamp at from 40–250 foot-candles. The image becomes easily visible in approximately 0.1 to 15 seconds although longer times may be used. In determining densities of the image and background, a reflection densitometer may be used (Macbeth Quanta Log Densitometer, Model RD-100). To test background stability, the light-developed image-record is exposed continuously to room light at 40 foot-candles for 16 hours. Speed in oscillography is measured in inches per second and is called writing speed. The radiation source in a typical instrument designed for the above writing papers is the Osram super high pressure arc lamp type HBO 107/1. Writing speeds are determined from the frequency of the signal and the peak-to-peak amplitude of the oscillation as recorded on the paper.

In order to illustrate the best mode of carrying out the invention, the following examples are given, but they are not intended to limit the scope of the invention.

In Examples I through V there was a time lag between image exposure and photolysis of at least 15 seconds.

EXAMPLE I

A gelatino-silver halide emulsion was prepared by slowly adding an aqueous solution containing a mixture of 1 mole of silver nitrate and 0.033 mole of plumbous nitrate to an aqueous gelatin solution containing 1 mole of potassium chloride and acidified with 0.05 mole of hydrochloric acid. The precipitation was carried out under a red safelight. The temperature at precipitation and for 40 minutes thereafter was held at 160° F. After precipitation, an aqueous solution of 1.6 moles of potassium bromide was added while the mixture was held at 160° F. The resulting emulsion was coagulated, washed and redispersed in the manner described in Example I of Moede U.S. 2,772,165. The redispersed emulsion was split into two equal portions (A and B) and held at 95° F. A solution of 4 grams of molecular iodine in 100 ml. ethanol was added to each portion in an amount to provide a concentration of 1 mole percent iodine based on the silver halide. To one emulsion portion (B), a sufficient amount of an aqueous acidic gold chloride solution was added

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to provide 0.05 mole percent of gold (Au^{+3}) based on the silver halide. To both emulsion portions there were then added the conventional hardeners, coating aids, etc. The emulsions were coated on a paper support to give a dry coating weight equivalent to 35 mg. AgBr/dm.². The coated emulsions were dried in a conventional manner.

Sample strips of both coatings were exposed for 100 microseconds through a 21-step, $\sqrt{2}$ wedge of a sensitometer (E.G. & G. Mark VII). The strips were light-developed by irradiation from a fluorescent lamp at an intensity of 40 foot-candles for 6 minutes. A second pair of strips were light-developed at an intensity of 250 foot-candles for 1 minute. The reflectance optical density of the resulting step wedge images was measured with the above-described densitometer.

The following data were obtained:

	Coating A ¹		Coating B ²	
Photolysis light intensity (foot-candles).....	40	250	40	250
Access time (seconds to first appearance of image).....	15	6	20	6
Net density at:				
Step 21 (D_{max}).....	.28	.17	.30	.21
Step 16.....	.18	.08	.27	.19
Step 8.....	.01	.00	.22	.08
Background density (photolytic fog).....	.20	.31	.18	.26
Image steps visible.....	15	10	21	17

¹ No gold.

² 0.05 mole percent Au^{+3} .

The rate of photolytic image growth and image quality was markedly superior for Coating B during all stages of light development.

EXAMPLE II

Example I was repeated except that an aqueous potassium iodide solution was substituted for the ethanolic molecular iodine solution and a sufficient amount was added to the silver chlorobromide emulsion to provide 2 mole percent potassium iodide based on the silver halide. Sensitometric testing gave results comparable to those obtained in Example I.

EXAMPLE III

A gelatino-silver chlorobromide emulsion was prepared as described in Example I, except that no plumbous nitrate was added to the aqueous silver nitrate solution. Molecular iodine and gold chloride were added to the redispersed emulsion as described in Example I to provide concentrations of 2 mole percent iodine and 0.05 mole percent Au^{+3} based on the silver halide. Sensitometric testing of sample strips of the coated emulsions gave the following results:

	Sample coatings	
Photolysis light intensity (foot-candles).....	40	250
Access time (seconds).....	6	1
Net density at:		
Step 21.....	.19	.16
Step 16.....	.18	.14
Step 8.....	.09	.05
Background density.....	.25	.31
Image steps visible.....	21	17

EXAMPLE IV

Example I was repeated except that sufficient molecular iodine and gold chloride were added to provide 4 mole percent iodine and 0.05 mole percent gold. The emulsion pH was adjusted to 4.5 before coating. Samples of the coating gave the following results:

	Sample coatings	
Photolysis light intensity (foot-candles).....	40	250
Access time (seconds).....	14	3
Net density at:		
Step 21.....	.29	.19
Step 16.....	.28	.18
Step 8.....	.22	.12
Background density.....	.22	.34
Image steps visible.....	20	17

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A third so-exposed strip was developed for one minute at room temperature in a conventional developer having the formula:

	Grams
1-phenyl-3-pyrazolidone -----	1.0
Hydroquinone -----	10.0
Sodium sulfite (anhydrous) -----	65.0
Sodium carbonate (monohydrate) -----	47.0
Benzotriazole -----	1.0
Water to make 1.0 liter.	

The developed strip was rinsed and then immersed for 5 minutes in a fixing solution having the following composition:

	Grams
Sodium thiosulfate (anhydrous) -----	153
Sodium sulfite (anhydrous) -----	15
Acetic acid, 28% -----	12
Potassium aluminum sulfate -----	20
Borax -----	18
Water to make 1.0 liter.	

After washing and drying, the strip showed a 13-step image having a maximum density of 1.08 against a white background.

EXAMPLE V

To the gelatino-silver chlorobromide emulsion of Example I sufficient molecular iodine and gold chloride were added to provide 2 mole percent of (I₂) and 0.1 mole percent of Au³⁺. In addition, aqueous potassium bromide and plumbous nitrate solutions were added to provide 4 mole

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rapidly became visible as a high-contrast, bluish-black trace against a pale yellow background. Exposed but unphotolyzed material was wet processed as described in Example IV to give a black trace image against a white background.

Photolyzed oscillographic traces when wet processed as in Example IV yielded reversed images, i.e., a white trace against a black background. There were high quality, high contrast images which duplicated the witting speed obtained with dry photolyzed images.

EXAMPLE VI

A gelatino-silver chlorobromide emulsion was prepared as described in Example I except that after coagulation washing the emulsion was redispersed in a solution containing 200 g. gelatin/mole silver salt, 4 mole percent KBr was added followed by the optical sensitizing dye, 3,3'-diethyl-5,5'-diphenyl oxacarbocyanine bromide, at 107 mg. per mole silver salt. Digestion followed for 40 minutes at 180° F. The emulsion was divided. Molecular iodine dissolved in ethylene glycol, auric chloride in dilute hydrochloric acid and a hardener and coating adjuvants added as indicated in the tables. The emulsions were coated on paper at 35 mg. AgBr/dm.².

The coated papers were exposed to a 10-microsecond xenon flash from an E.G. & G. Mark III sensitometer through a stepwedge, half covered with a Wratten #4 (Yellow) filter. Photodevelopment followed immediately under white fluorescent lights at 50 foot candles for 5 minutes. Results are listed in the following table:

Coating No.	Sensitizing dye, mg./mole	I ₂ , mole percent	Au ³⁺ , mole percent	Access time, sec.	Speed, visible √2 steps		Reflection den.		
					White	Yellow	D _{max.}	D _{min.}	Δ
1-----	107	2.0	0.05	16	14	7	0.73	0.42	0.31
2-----	107	1.0	0.05	17	14	10	.71	.40	.31
3-----	107	0.5	0.05	19	13	10	.67	.41	.26
4-----	107	2.0	0.02	18	13	7	.74	.43	.31
5-----	107	2.0	0.01	18	13	6	.73	.44	.29

percent and 2 mole percent respectively, all based on the silver halide. The emulsion was adjusted to a pH of 2.8 just prior to coating. Sample strips gave the following sensitometric results:

	Sample coatings	
Photolysis light intensity (foot candles)-----	40	250
Access time (seconds)-----	25	5
Net density at:		
Step 21-----	.32	.29
Step 16-----	.31	.30
Step 8-----	.20	.14
Background density-----	.20	.28
Image steps visible-----	20	17

A third strip was wet processed as described in Example IV to yield a 14-step image having a maximum density of 1.27 against a white background.

The coated material was also exposed in a commercial

EXAMPLE VII

A gelatino-silver chlorobromide emulsion was prepared as described in Example I except that coagulated and washed curds were dispersed in an aqueous solution containing 160 g. gelatin/mole silver salt. Sodium hydroxide was added to give pH 7.15 after stirring 60 min. at 95° F. Sensitizing dyes were added and the emulsion digested 65 min. at 140° F. At 95°, molecular iodine at 0.2 mole percent and auric chloride at 0.01 mole percent based on the silver were added followed by hardener and coating adjuvants. The dyes were 2,2'-diethylthiacyanine iodide (A), a cyanine, 3,3'-diethyl-5,5'-diphenyl-9-ethyl-oxacarbocyanine (B), a carbocyanine and 5-(3-methyl-2-thiazolynylidene-isopropylidene)-3-ethylrhodanine, (C) a merocyanine.

Sensitometry was carried out as in Example VI except that a Wratten #8(K2) filter replaced the Wratten #4.

Coating No.	Dye	AgClBr mg. dye/mole	I ₂	Au ³⁺	Access time, sec.	Speed, visible √2 steps		Reflection den.		
						White	K ₂	D _{max.}	D _{min.}	Δ
1-----	(B)-----	67	0.2	0.01	22	15	9	0.41	0.23	0.18
	(A)-----	67	0.2	0.01						
2-----	(B)-----	133	0.2	0.01	17	16	12	.45	.22	.23
	(A)-----	67	0.2	0.01						
3-----	(C)-----	67	0.2	0.01	13	15	13	.45	.23	.22
4-----	No dye-----		0.2	0.01	18	13	1	.39	.20	.19

EXAMPLE VIII

A gelatino-silver chlorobromide was prepared in the same manner as in Example VII except that 0.01% Au³⁺ was added before dye (C) of Example VII (67 mg./mole AgX) and the emulsion then digested 90 min. at 140° F.

oscillographic recorder using the above-described Osram 70 lamp as a light source. With a paper speed of 160 inches per second, the sample material recorded a 6000 cycles per second signal at writing speeds in excess of 50,000 inches per second. When photolyzed under room fluorescent lights at about 80 foot-candles intensity, these traces

The emulsion contained hardener and a coating adjuvant during digestion. Potassium iodide was added at several levels and the emulsion was coated on paper base.

Sensitometry was carried out as in Example VII.

Coating No.	Dye (C) mg./μ	Mole percent		Access time, sec.	Speed, visible steps		Reflection den.		
		Au ⁺	KI		White	K ₂	D _{max}	D _{min}	Δ
1	67	0.01	0.0	28	15	11	0.27	0.20	0.07
2			0.38	20	13	11	.38	.23	.15
3			0.79	16	13	10	.38	.23	.15
4			1.67	13	13	10	.36	.22	.14
5			2.63	15	13	9	.36	.22	.14

EXAMPLE IX

The coated emulsion described in Example VII was exposed to a 10-microsecond xenon flash, E.G. & G. Mark III sensitometer. Within 10 seconds, the sample was exposed to 50 foot-candle, white fluorescent lamps for 10 seconds through a $\sqrt{2}$ step-wedge placed so that half of the wedge covered the flashed area and half covered a previously unexposed area. The coating was then conventionally developed under safelights for 60 seconds at 68° F. in an open tray containing the developer shown in Example IV followed by fixing and washing. Reflection densities gave the following:

1st exposure, mcs.	2d exposure, mcs.	Image area, refl. density	Back-ground, refl. density	Image over back-ground
0	0	0.19	0.20	-----
28	0	1.21	0.20	1.01
28	5.5	1.21	0.20	1.01
28	11.0	1.21	0.29	0.92
28	21.0	1.14	0.43	.71
28	41	0.60	0.53	.07
28	82	0.29	0.55	-.26
28	165	0.19	0.57	-.38
28	330	0.19	0.56	-.37
28	660	0.19	0.55	-.36
28	1,325	0.19	0.54	-.35
28	2,750	0.19	0.53	-.34
28	5,500	0.19	0.52	-.33

EXAMPLE X

A coating was prepared as described in Example VI labeled No. 3. Exposure was made to a 10-microsecond xenon flash from an E.G. & G. Mark III sensitometer through a $\sqrt{2}$ step-wedge. After a period of 10 seconds in the absence of actinic radiation, the coating was given a second exposure of 10 seconds to white fluorescent lamps of 50 foot-candle intensity passed through a Wratten #16 gelatin filter to remove light absorbed by the silver halide grains but not by the dye. The filter was then removed and photodevelopment to white lamps of 50 foot-candles proceeded until a usable image was obtained. An increase in image density and speed was obtained in the portion under the Wratten #16 filter. This technique, called dye latensification was first described in U.S. 3,183,088, H. D. Hunt, May 11, 1965.

	Density with 10 sec. dye latensification	Density with no dye latensification
Step 21	0.52	0.50
Step 16	.45	.43
Step 12	.39	.37
Step 8	.33	.32
Background	.32	.32
Visible steps	14	13

EXAMPLE XI

Sample strips of the coating described in Example V were exposed as described in Example I. These were held in total darkness for increasing time intervals before

being photolyzed as described in Example I. The following results were obtained:

Photolysis light intensity: 100 foot-candles

Photolysis time: 4 minutes

Temperature: 68° F.

TIME DELAY BETWEEN EXPOSURE AND PHOTOLYSIS

Seconds	2	10	30	60	180
Net density at step:					
21	.39	.39	.39	.41	.40
16	.30	.33	.34	.36	.37
12	.22	.24	.29	.32	.35
8	.12	.13	.17	.20	.23
4	.02	.01	.02	.01	.03
Background density	.27	.28	.29	.30	.29

A similar experiment was performed except that the exposed strips were heated at 100° F. for increasing time intervals after exposure. Heat was then removed and the strips photolyzed as above.

PREHEAT TIME AT 100° F.

Seconds	0	1	2	5	10
Net density at step:					
21	.34	.34	.41	.40	.41
16	.28	.31	.37	.39	.39
12	.22	.24	.33	.34	.35
8	.11	.13	.23	.24	.24
6	.06	.08	.13	.15	.14
Background density	.27	.27	.28	.28	.28

In place of the gelatin binding agent used in the foregoing examples, there can be substituted synthetic water-permeable organic colloid binding agents. Such agents include water-soluble or permeable polyvinyl alcohol and its derivatives, e.g., partially hydrolyzed polyvinyl acetates, polyvinyl ethers, and acetals containing a large number of extralinear $-\text{CH}_2\text{CHOH}-$ groups, hydrolyzed interpolymers of vinyl acetate and unsaturated addition polymerizable compounds, for example, maleic anhydride, acrylic and methacrylic acid esters and styrene. Suitable colloids of the last mentioned type are disclosed in U.S. Pats. 2,276,322, 2,276,323, and 2,397,866. The useful polyvinyl acetals include polyvinyl acetaldehyde acetal, polyvinyl butyraldehyde acetal, polyvinyl butyraldehyde acetal and polyvinyl sodium o-sulfobenzaldehyde acetal. Other useful colloid binding agents include the polyvinyl lactams of Bolton U.S. 2,495,918, e.g., poly-N-vinyl pyrrolidone; the hydrophilic copolymers of N-acrylamido alkyl betaines of Shacklett U.S. 2,833,650 and hydrophilic cellulose ethers and esters.

Suitable supports for the novel photographic emulsions of this invention include those in the prior art for light-writing and oscillographic recording. The preferred support is photographic grade paper but may be of any material suitable for coating photographic emulsions such as cellulose ester films and the film base materials disclosed in Alles et al. U.S. 2,627,088 and Alles U.S. 2,779,684 and

polystyrene. Where paper is used, brightening agents of the triazinyl stilbene type compounds may be incorporated either in the emulsions or in the papers.

The novel feature of obtaining a synergistic effect by incorporating molecular iodine or an iodide salt and a gold salt into a silver halide emulsion after the precipitation stage either with or without the addition of lead salts at precipitation and with the addition of excess bromide ions produces photolyzable, direct-writing, photosensitive emulsion layers having certain advantages over the prior art products. In addition to being extremely convenient to use because wet processing can be eliminated, it is also adaptable to conventional chemical development where it is desired. The invention also provides an element wherein one may obtain a reversal image by the proper combination of photolysis and chemical processing. The invention also provides an element wherein one may subject the exposed material to relatively high illumination for long periods of time or use the material to photographically reproduce the image record using high intensity exposing radiation without serious image deterioration. The elements of this invention have high photographic speed and permit rapid access to the recorded image. They also provide images having high maximum density and image stability. In addition, background densities are markedly lower which enhances the contrast of photolyzed images. Still further advantages will be apparent from the foregoing description.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A light-developable, direct-writing, light-sensitive silver halide emulsion layer comprising silver halide grains having an average grain size of 0.1–10 microns dispersed in a water-permeable macromolecular organic colloid having protective colloid properties, said layer containing, based on the silver halide:

- (a) 0.05–15 mole percent of molecular iodine or an iodide ion-yielding compound,
- (b) 0.0005–1.0 mole percent of a gold salt.
- (c) 0–120 mole percent of a water-soluble bromide, and/or
- (d) 0–5 mole percent of a water-soluble plumbous salt;

the iodine or iodide and the gold salt forming an active gold-iodine complex on or near the surfaces of the silver halide grains.

2. An emulsion layer according to claim 1 containing 0.8–10 mole percent of iodine or iodide ion-yielding compound and 0.01 to 0.2 mole percent of the gold salt.

3. An emulsion layer according to claim 1 wherein the silver halide grains are silver chlorobromide grains and said colloid is gelatin.

4. A photographic element comprising a sheet support having on at least one surface a light-developable, direct-writing, light-sensitive silver halide emulsion layer comprising silver halide grains having an average grain size of 0.1–10 microns dispersed in a water-permeable macromolecular organic colloid having protective colloid properties, said layer containing, based on the silver halide;

- (a) 0.05–15 mole percent of molecular iodine or an iodide ion-yielding compound,
- (b) 0.0005–1.0 percent of a gold salt,
- (c) 0–120 mole percent of a water-soluble bromide, and/or
- (d) 0–5 mole percent of a water-soluble plumbous salt;

the iodine or iodide and the gold salt forming an active gold-iodine complex on or near the surfaces of the silver halide grains.

5. An element according to claim 4 wherein said support is paper.

6. An element according to claim 4 containing 0.8–10 mole percent of iodine or iodide-yielding compound and 0.01 to 0.2 mole percent of the gold salt.

7. An element according to claim 4 wherein the silver halide grains are silver chlorobromide grains and said colloid is gelatin.

8. An element according to claim 4 wherein the silver halide emulsion forms latent images predominantly in the silver halide grains that have been formed in the presence of plumbous ions.

9. An element according to claim 4 wherein the silver halide grains are formed before addition of plumbous ions.

10. An element according to claim 4, wherein the emulsion contains an optical photographic silver halide sensitizing dye to extend the sensitivity of the silver halide grains.

11. A process of forming images which comprises exposing to a source of intense actinic radiation to form an image, a light-developable, direct-writing, light-sensitive silver halide emulsion layer comprising silver halide grains having an average grain size of 0.1–10 microns dispersed in a water-permeable macromolecular organic colloid having protective colloid properties, said layer containing, based on the silver halide:

- (a) 0.05–15 mole percent of molecular iodine or an iodide-yielding compound,
- (b) 0.0005–1.0 percent of a gold salt to form on or near the surfaces of the grains a gold-iodine complex,
- (c) 0–120 mole percent of a water-soluble bromide, and/or
- (d) 0–5 mole percent of a water-soluble plumbous salt;

and photodeveloping the exposed silver halide layer with actinic radiation of less intensity than the exposing radiation until an image is formed.

12. A process according to claim 11 wherein actinic radiation is excluded from the exposed layer for $\frac{1}{10}$ to 180 seconds to autolatensify the layer between the step of exposing the layer to intense radiation and the step of photodeveloping the autolatensified layer.

13. A process according to claim 11, wherein the exposed layer is heated to a temperature above room temperature, but not more than 200 F. during the period of excluding actinic radiation from the layer.

14. A process according to claim 11, wherein the image formed is then developed to form a reverse image with a solution containing a silver halide developing agent, and the resulting developed reverse image is fixed with a solution containing a silver halide fixing agent.

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